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A STUDY OF THE CONDUCTIVITY OF CERTAIN ORGANIC  
SALTS IN ABSOLUTE ETHYL ALCOHOL AT  
15°, 25° AND 35°

by

ARTHUR McCAY PARDEE

DISSERTATION

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ACKNOWLEDGMENT.

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The investigation under discussion in this dissertation was suggested by the late Professor H.C.Jones and was under his direct supervision up to the time of his death. The writer embraces this opportunity to pay a high tribute to the memory of this teacher who inspired his men with enthusiasm and led them by an example of tireless energy and close concentration towards a more thorough understanding of the fundamental truths of science. It is a pleasant duty to express an appreciation for the valuable instruction, inspiration and counsel which he has received both in the lecture room and in the laboratory from Professors Morse, Remsen and Swartz, and Associate Professors Lovelace, Frazer and Reid.

The author wishes to express his gratitude to Dr. H.H. Lloyd, his coworker, who has contributed much to the solution of the problems that have been encountered in the course of this investigation.

Dr. P.B.Davis has rendered valuable assistance in the designing and construction of apparatus necessary for this work, and for such the author feels his sense of obligation.



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15°, 25° AND 35°.

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INTRODUCTION.

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For some years past a comprehensive study has been made in this laboratory of the electrical conductivity and dissociation of various organic acids in aqueous solution <sup>1</sup>. This naturally led to the investigation of the organic acids in absolute alcohol. Wightman, Wiesel and Jones <sup>2</sup>, and Lloyd, Wiesel and Jones <sup>3</sup> undertook a thorough study of this latter work.

On account of their inability to obtain  $\Delta\sigma$ . for these acids experimentally, it was perfectly logical that the behavior of the organic salts in absolute alcohol be investigated. We have developed this for two reasons; first, we believe that accurate conductivity data on these compounds

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1. Carnegie Inst. Wash. Pub. No. 170, Part II; No. 210, Chap. II.

2. Carnegie Inst. Wash. Pub. No. 210, Chap. III; J. Amer. Chem. Soc. 36, 2243 (1914).

3. Carnegie Inst. Wash. Pub. No. 230, Chap. VII; J. Amer. Chem. Soc. 38, 121 (1916).



is of value in the general consideration of the whole subject; secondly, we are interested in such minor questions as temperature coefficients of conductivity, conductivity in relation to chemical constitution, limits of experimental accuracy in working with dilute alcoholic solutions, and the general phenomena of alcoholysis.

We realize also that here might be a method for obtaining the equivalent conductivity at infinite dilution, ( $\Lambda_0$ ), for the organic acids previously studied, by experimentally developing the  $\Lambda_0$  for the salts and from this the migration velocities of the anions. Once obtaining this data for the anions, it could be introduced into the Kohlrausch equation for determining  $\Lambda_0$  theoretically, as demonstrated possible for aqueous solutions by Ostwald <sup>4</sup>.

With the values of  $\Lambda_0$  for both acids and salts, it is of course possible to determine percentage dissociation values as well as affinity constants for the acids in question.

#### HISTORICAL.

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The phenomena of the electrical conductivity of the sodium salts of organic acids in absolute alcohol up to the present time have received but scant attention. With few

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4. *Zeit. physik. Chem.* 2, 561 (1888); 3, 170 (1889);  
*Amer. Chem. Journ.* 46, 66 (1911).



exceptions all investigations that have been made were incidental in nature and were chosen simply as a type of the organic salts.

Dutoit and Rappeport <sup>5</sup>, in a study on the limiting conductivities of some electrolytes in absolute alcohol, measured among other salts sodium acetate, evidently taking the same as an example of the salts of organic acids. They subjected their results to some rather interesting deductions but unfortunately their conductivities were measured at 18°, making exact comparison with those at 25° an impossibility. They interpreted their results in a manner similar to that done by Goldschmidt, and so their deductions are really illustrated in the latter's communications.

Dhar and Bhattacharyya <sup>6</sup> carried on some work in alcohol with various salts and studied among others the following organic derivatives: sodium propionate, sodium benzoate and sodium salicylate. Their measurements at odd concentrations and temperatures render comparison impossible.

Heinrich Goldschmidt <sup>7</sup>, incidental to his study of the esterification of organic acids in absolute alcohol, found it necessary to measure the conductivities of a number of sodium salts of these acids. The preparation of the absolute

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5. Jour. Chim. Phys. 6, 545 (1908).

6. Zeit. anorg. Chem. 82, 357 (1913).

7. Zeit. physik. Chem. 89, 129 (1914); 91, 46 (1916).



alcohol used by him is of interest. Ordinary 95 per cent. alcohol was allowed to stand in contact with lime for some time and then distilled. The process was repeated, this time using a copper distilling vessel and condenser. Thus the water content was reduced to 0.003 normal or 0.06 gr. per liter. If completely anhydrous alcohol was desired, this product was treated finally with metallic calcium. For this purpose calcium bars were turned on a lathe to remove the coating of hydroxide, and the bright metal was cut into pieces the size of a pea. An amount of calcium equal to ten times the amount of water present (about 0.1 gr.) was introduced into the alcohol. The whole was then heated for several hours with a reflux condenser attached, and a rapid stream of dry air was circulated through the distillation chamber to remove traces of ammonia. In this way absolute alcohol was obtained having a specific conductivity of  $2 \times 10^{-7}$ .

Having procured alcohol of sufficient purity, Goldschmidt measured the conductivities of certain organic salts at 25°. The salts were made, according to his bare statement, by neutralizing the alcoholic solution of the acids with an alcoholic solution of sodium ethylate made by dissolving metallic sodium in absolute alcohol. Robertson and Acree<sup>8</sup>

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8. Robertson, Dissertation, J. H. U., 1913.



describe accurately their method for preparing and standardizing this reagent in work which was carried out at a much earlier date than this. Goldschmidt does not mention the fact that he titrated his acids in alcohol against the standard ethylate. The inference is that he standardized the ethylate by titration with an aqueous solution of a standard mineral acid using methyl orange as an indicator, and then added arbitrarily the theoretical amount necessary to a certain definite weight of the organic acid in alcoholic solution. He gives no experimental proof or statement as to whether he had tested the purity of the acids used. Although it has been shown that such an assumption is possible in the majority of cases, it is not always true and we have shown it necessary to titrate the acid before using the same. A further discussion of this is to be found in the experimental part of this paper.

Goldschmidt measured the conductivities from N/10 to N/5120 concentrations, and the values determined for five different salts are shown below. These results are given to enable us to discuss them and the deductions leading from them, as well as to point out later wherein we differ from him as to certain conclusions. These salts are sodium trichloroacetate, dichloroacetate, picrate, salicylate and sulfosalicylate. There is appended with each table his calculation for  $\Delta_0$  of the salt at specified dilutions.



Table I.

9

Sodium Trichloroacetate.

| V.   | $\Delta$ I. | $\Delta$ II. |                               |
|------|-------------|--------------|-------------------------------|
| 10   | 11.07       | -            |                               |
| 20   | 13.95       | -            |                               |
| 40   | 17.27       | 17.33        | $\Delta_o(320-1280) = 46.10$  |
| 80   | 20.99       | 20.96        | $\Delta_o(640-2560) = 46.20$  |
| 160  | 24.94       | 25.12        | $\Delta_o(1280-5120) = 45.52$ |
| 320  | 28.83       | 29.04        |                               |
| 640  | 32.39       | 32.50        |                               |
| 1280 | 35.28       | 35.29        | Mean $\Delta_o = 46.00$       |
| 2560 | 37.61       | 37.48        |                               |
| 5120 | 39.23       | 38.92        |                               |

Table II.

Sodium Dichloroacetate.

| V.   | $\Delta$ I | $\Delta$ II | $\Delta$ III |                                  |
|------|------------|-------------|--------------|----------------------------------|
| 10   | -          | -           | 9.85         | I $\Delta_o(320-1280) = 48.54$   |
| 20   | -          | -           | 12.64        | $\Delta_o(640-2560) = 49.43$     |
| 40   | 16.11      | 15.95       | 15.86        | $\Delta_o(320-1280) = 47.68$     |
| 80   | 19.78      | 19.59       | 19.53        | II $\Delta_o(640-2560) = 48.36$  |
| 160  | 23.78      | 23.65       | 23.54        | $\Delta_o(1280-5120) = 50.64$    |
| 320  | 28.00      | 27.70       | 27.52        |                                  |
| 640  | 31.96      | 31.51       | 31.49        |                                  |
| 1280 | 35.66      | 34.87       | 34.96        | III $\Delta_o(320-1280) = 47.36$ |
| 2560 | 38.42      | 37.74       | 38.02        | $\Delta_o(640-2560) = 44.14$     |
| 5120 | -          | 40.71       | 40.86        | $\Delta_o(1280-5120) = 50.40$    |
|      |            |             |              | $\Delta_o$ taken = 52.           |



Table III.  
Sodium Salicylate.

| V    | $\Delta$ . |
|------|------------|
| 16   | 9.57       |
| 20   | 12.21      |
| 40   | 15.27      |
| 80   | 18.78      |
| 160  | 22.67      |
| 320  | 26.58      |
| 640  | 30.14      |
| 1280 | 33.20      |
| 2560 | 35.48      |
| 5120 | 36.29      |

Table IV.  
Sodium Sulfosalicylate.

| V    | $\Delta I$ | $\Delta II$ | $\Delta_{mean}$ |
|------|------------|-------------|-----------------|
| 40   | 13.56      | 13.54       | 13.5            |
| 80   | 16.72      | 16.74       | 16.7            |
| 160  | 20.21      | 20.18       | 20.2            |
| 320  | 23.76      | 23.69       | 23.7            |
| 640  | 27.06      | 27.02       | 27.0            |
| 1280 | 30.0       | 30.03       | 30.0            |
| 2560 | 32.22      | 32.23       | 32.2            |
| 5120 | 33.84      | 34.12       | 34.0            |



Table V.

| <u>Sodium Picrate.</u> |                               |                                |
|------------------------|-------------------------------|--------------------------------|
| <u>V</u>               | <u><math>\Delta</math> I.</u> | <u><math>\Delta</math> II.</u> |
| 40                     | 18.04                         | 18.14                          |
| 80                     | 22.06                         | 22.11                          |
| 160                    | 26.34                         | 26.34                          |
| 320                    | 30.61                         | 30.64                          |
| 640                    | 34.59                         | 34.59                          |
| 1280                   | 37.94                         | 38.07                          |
| 2560                   | 40.43                         | 40.65                          |
| 5120                   | 42.03                         | 42.75                          |

$$\bar{I} \begin{cases} \Delta_o / (320 - 1280) = 50.42 \\ \Delta_o / (640 - 2560) = 50.10 \\ \Delta_o / (1280 - 5120) = 48.99 \end{cases}$$

$$\bar{II} \begin{cases} \Delta_o / (320 - 1280) = 50.72 \\ \Delta_o / (640 - 2560) = 50.97 \\ \Delta_o / (1280 - 5120) = 50.72 \end{cases}$$

Selected  $\Delta_o = 51$ .

Goldschmidt thought that it was evident, after carrying his dilutions to 5120 liters, that  $\Delta_o$  could not be reached by ordinary experimental methods. He attempted to calculate  $\Delta_o$  for these organic salts and expected to obtain the relative velocity of the organic anion from the salt, and introduce the same into the equation -

$$\Delta_o = c + a$$

To determine  $\Delta_o$  for the organic salt he made use of the Kohlrausch formula<sup>9</sup> -

$$\Delta_o = \bar{A} + a \sqrt[3]{\frac{1}{V}}$$

in which  $\Delta_o$  is an unknown,  $\bar{A}$  the conductivity at a



known dilution,  $v$ , and a an unknown constant. Two equations involving the use of different  $\Delta$  values are equated, the  $\Delta_0$  being the same in both cases, and the expression solved for the value a. Once having this, it is a simple matter to solve for  $\Delta_0$  in one of the two original equations. By reference to the tables quoted above we can observe how such values are derived. It is to be noticed that alternate  $\Delta$  values are equated. This is done so that the difference may be of sufficient degree of magnitude and that any inaccuracy in an individual measurement may not affect two successive derivations.

A glance at the tables and calculations will show that the calculated values for  $\Delta_0$  are by no means concordant. The higher the value of  $\Delta$  used in the equation, the lower becomes the calculated  $\Delta_0$ . His final conclusions are vague and must be regarded as only approximate and inconclusive. He generally chose the highest possible.

Goldschmidt seems to disregard entirely the very exact and admirable piece of work done on the subject of the limiting conductivity and degree of ionization of alcoholic solutions by B.B.Turner <sup>10</sup> in this laboratory. Turner carried his dilutions to far greater limits, as the following table illustrates.

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10. Amer. Chem. Journ. 40, 558 (1908).



We have repeated this work and have every reason to believe that it is unquestioned and is remarkably accurate especially when one considers that it was done without the

Table VI.

KI in Absolute Alcohol  
Conductivity in mhos at 25°.

| V        | $\Delta$ |
|----------|----------|
| 10       | 22.2     |
| 12       | 23.0     |
| 16       | 24.1     |
| 32       | 27.5     |
| 64       | 31.1     |
| 128      | 35.0     |
| 250      | 38.2     |
| 500      | 41.4     |
| 1000     | 44.0     |
| 5000     | 47.8     |
| 10000    | 48.4     |
| 20000    | 48.5     |
| $\infty$ | 48.5±0.5 |

more recent conductivity apparatus now at our disposal.

Turner showed that up to 5000 liters dilution it is easy to obtain concordant results; but the values for  $\Delta$ .



as calculated according to the Kohlrausch method are not constant for these higher dilutions. Like those of Goldschmidt, they decrease the higher the values of  $\Lambda$  used in the equation. Turner also showed that plotting  $\Lambda$  against the reciprocal of the cube root of the volume does not give a straight line as in aqueous solutions of equal dilutions, but rather a smooth curve slightly convex towards the dilution axis. He therefore assumed that the Kohlrausch method fails to answer the requirements of absolute alcoholic solutions. Extrapolation of his results with the formula would give a value of 56 for  $\Lambda_0$  instead of the experimental value of 48.5 obtained. He thought that accidental introduction of water into his solutions might affect the readings, so to test this he added as much as 0.2 to 0.3 % of water by weight to his alcoholic solutions, with a variation in conductivity of only  $0.01 \times 10^{-6}$  units, showing that no accidental experimental error of this nature had crept in.

Furthermore, Dutoit and Rappeport <sup>5</sup> showed identically the same phenomena with a number of inorganic salts in work to which reference has already been made (page 6). This work like that of Turner's seems to have escaped the notice of Goldschmidt, as he does not mention either piece of work in any of his papers.

In other words, the problem as undertaken by Goldschmidt



is very incomplete from this standpoint. No reason can be given why he should use arbitrarily chosen limits for  $v$  in applying the Kohlrausch formula, nor is it shown how accurately measured conductivities up to 20000 liters dilution can be reconciled with such a falling off in the calculated  $\Delta_0$  for the salt.

Whether such a method could be applied or not, or whether another can be substituted in its place, is a question of very great importance. Furthermore, Goldschmidt based his conclusions on the results of only six or seven salts. It was therefore deemed advisable by the present writer that in the first place more conductivity data on a larger number of salts be obtained, and in the second place, these measurements be made at several temperatures in order to look at this subject in a broad way.

Such was the state of the problem at the inception of the experimental work on this dissertation.

#### EXPERIMENTAL.

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##### Reagents.

The alcohol used in this investigation was prepared in the following manner. Ordinary 95 per cent. ethyl alcohol was heated for several days with lime in a copper tank with a glass condenser attached. A minimum of refluxing in the



condenser was obtained by inserting into the tank through the stopper a coil of 3/16 inch lead pipe containing running water and serving to cause condensation immediately below the reflux tube. The alcohol was distilled off using a glass still head with a bulb blown in it and containing glass wool soaked in alcohol in order to prevent any dusting over of the dry calcium hydroxide. The middle fraction was treated in the same manner as above and again fractionated. This process was continued until a specific gravity of 0.78507 was obtained, the extreme limits of variation being 0.78505 to 0.78510, which according to Circular # 19 of the Bureau of Standards corresponds to a purity of from 100 to 99.987 per cent. The specific conductivities of the alcohol varied with the different samples from 0.46 to  $1.6 \times 10^{-7}$  mhos. Upon the final distillation the alcohol was collected in a six liter, alcohol extracted, Jena bottle with a sealed stopper carrying a siphon for drawing off the liquid, a calcium chloride - soda lime tube and an adapter with a ground glass stopcock. Alcohol prepared and stored in this manner, after several days following the distillation remained practically unchanged as to its conductivity for a period of several weeks. It was found that our discarded alcoholic solutions and washings, when distilled once in glass with a few drops of concentrated sulfuric acid before the final lime treatment, produced a very



superior grade of absolute alcohol, being generally better than that obtained from fresh supplies of the 95 per cent. material.

The organic salts used in this investigation were prepared by adding the necessary amount of sodium ethylate in absolute alcohol to the organic acid in alcoholic solution, as advised by Goldschmidt and previously mentioned in the historical section (page 7). The acids employed were taken from the various samples purified in the work of Lloyd, Wiesel and Jones. When such were lacking new material was obtained from well-known firms and purified in the following manner. Whenever possible the acid was precipitated from hot alcoholic solution, but when necessary a small amount of water was added. In every case the fractionation was carried out several times. The halogen substituted aliphatic acids were fractionally crystallized from hot benzol, placed in a sulfuric acid dessicator, and the final traces of the benzol removed by introducing into the container pieces of paraffine which acted as an absorbant for the solvent. To purify the liquid aliphatic acids we resorted to both fractional crystallization by means of a refrigerant and repeated distillations under reduced pressure, in the latter case collecting the various fractions in a specially constructed receiver for small quantities.

The ethylate was prepared as needed in the following



manner, as suggested by J. H. Shrader <sup>11</sup>. A special grade of metallic sodium, free from other metals, was wiped carefully with filter paper, the approximate amount was pared to fresh surfaces, and in small pieces was placed first in a good grade of alcohol, then transferred into some conductivity alcohol for final washing, and finally dropped into a measuring flask of the best alcohol, so that upon solution it could be made up to the mark. With practice it was possible to estimate successfully the amount of sodium to produce a nearly N/10 solution. This solution was standardized and used within an hour or two for the salt preparation. It was found necessary to make the ethylate to be used immediately, as evidences of decomposition giving a straw color to the solution appeared within twenty four hours of its preparation, and even sooner in the case of more concentrated solutions.

This ethylate solution was immediately standardized by means of a N/10 aqueous solution of hydrochloric acid. This latter reagent was prepared by the method of Hulett and Bonner <sup>12</sup>, lately extended by Hendrixson <sup>13</sup>. As a check on this solution four series of silver chloride gravimetric analyses were made at various times throughout the

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11. J. H. Shrader, Dissertation, J. H. U., 1913, p. 14-16.

12. J. Amer. Chem. Soc. 31, 390 (1909).

13. J. Amer. Chem. Soc. 37, 2352 (1915).



year, none of which varied more than 0.1 of 1 per cent.

Phenolphthalein served as the indicator for the various titrations, special precautions - noted in a later paragraph - being used to prevent the interference of carbon dioxide from the atmosphere. As a final proof of the correctness of our choice of indicators the ethylate was standardized with hydrochloric acid using in this case methyl red as an indicator, and it showed results concordant with the phenolphthalein values previously obtained. The methyl red naturally was useless in the titration of most of the organic acids, so its use was abandoned after proving the value of the phenolphthalein procedure.

In order to dry completely our various pieces of apparatus, acetone was used, as suggested by Barnebey<sup>14</sup>. The acetone was dehydrated over calcium chloride and then redistilled.

#### Apparatus.

The cylindrical type of conductivity cells was used in all save the more concentrated solutions, where the ordinary plate type was adopted. The reason for using the cylindrical cell lies in the fact that the organic salts in absolute alcohol, although having more conductivity than the organic acids, are nevertheless of sufficient resistance

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14. J. Amer. Chem. Soc. 37, 1835 (1915).



to warrant such a procedure. White <sup>15</sup> and Wightman <sup>16</sup> have described the method for obtaining the constants of these cells.

Both the temperature coefficients of expansion of alcohol and the temperature coefficients of conductivity of substances in it as a solvent are so large that it was especially necessary to maintain the solutions at a constant temperature to within  $0.01^{\circ}$ . The thermometers were of the differential Beckmann type and were carefully compared with a standard Reichsanstalt instrument which had in turn been calibrated at the Bureau of Standards. The gas regulator and thermoregulator combined was devised by Davis and Hughes <sup>17</sup>. The improved form of constant temperature bath as devised by Davis <sup>18</sup> was used in our investigation. These baths are capable of even finer temperature adjustment than that stated above as employed in our work.

The resistance box used throughout this work was calibrated at the Bureau of Standards. The improved Kohlrausch slide wire bridge was employed by means of which it was possible to read distances on the slide wire corresponding to tenths of a millimeter (the total length of the wire

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15. Amer. Chem. Journ. 42, 527 (1909).

16. Amer. Chem. Journ. 44, 64 (1911).

17. Zeit. physik. Chem. 85, 519 (1913).

18. Carnegie Inst. Wash. Pub. No. 210, p. 21 (1914).



being five meters). Special precautions were taken to remove all external resistance in the circuit. Number 10 B. & S. insulated copper wire was used, with all leads coming to the bridge dipping into a mercury contact rocking commutator.

In the volumetric work Jena flasks were employed (50, 100, 200, 250, 500, 1000 c.c.) which had been previously calibrated in this laboratory and recalibrated by ourselves using weight methods. Reichsanstalt double mark pipettes were recalibrated before use. In filling and draining the pipette the following device was suggested by Dr. Davis. It consisted of a right-angled T-tube with a glass stopcock on the base of the T, the pipette being attached by rubber to one end of the cross piece held vertically with the regulating finger on the opposite end of the cross piece. The control finger is maintained throughout the operation at this opening and the danger of contamination by suction is removed. A calcium chloride - soda lime tube is inserted in the rubber tube leading from the glass stopcock on the base of the T to the mouth, for obvious reasons. The 50 c.c. burettes adopted were calibrated at 2 c.c. intervals by weight.

In order to titrate with phenolphthalein in an atmosphere free from carbon dioxide the following apparatus was constructed partially as suggested by Hendrixson <sup>13</sup>.



A carboy was connected to an ordinary tire pump and served as a gas reservoir. The air was led through three wash bottles, the first containing concentrated potassium hydroxide solution, the second a more dilute solution and the third pure water. The titration was effected in an Erlenmeyer flask closed with a rubber stopper which in turn was fitted loosely around the burette tip serving in this way as a vent for the stream of air passed slowly through the solution.

The difficulty in dessicating our acids when once purified was solved by means of a vacuum drying oven designed by Dr. Davis and myself. This apparatus consisted of a bell-jar 18 cm. by 24 cm. with a rubber stopper at the top in which was inserted a thermometer and the evacuating connection. This tubulated ball-jar was placed on a heavy iron vacuum plate and when in use the two parts were sealed by means of rubber cement. Leading into the plate by means of a rubber stopper from below were placed four wires; one pair to a 110 volt 50 watt 16 candle power carbon filament lamp placed in a metal chimney, and the other pair leading to a miniature fan motor running on 110 volt direct current with an eight candle power carbon filament lamp in series with it outside the jar. The external electrical connections were made to enable the control of both heat and power separately. Within the oven circulation was obtained



by means of the fan driving towards the open base of the brass chimney. Drying was facilitated by means of two dishes containing either concentrated sulfuric acid or phosphorous pentoxide. The material was dried on watch crystals placed on a perforated tray or shelf set above the motor and lamp chimney. At 90 mm. pressure we were enabled to get a boiling-point for water of  $49.6^{\circ}$ . Since the lamp heating unit maintained a temperature of  $65^{\circ}$  it is easily seen that with the added help of a strong dehydrating agent all traces of the crystallizing solvent were removed. In proof of this practically all the organic acids titrated theoretical. This piece of apparatus has the following advantages: ease of construction, ability to be evacuated sufficiently with the common water suction pump, and the requirement of a lighting current for operation. Furthermore, it is convenient to have all parts of the apparatus exposed to view through the transparent bell-jar, and to open the oven it is only necessary to break the rubber cement seal around the base of the jar.

#### Procedure.

The sodium ethylate prepared as previously described was standardized by titration with N/10 HCl in a carbon dioxide freed atmosphere as described previously. When the ethylate was standardized the organic acid from which the



salt was to be made was weighed out in quantity sufficient to give 100 c.c. N/10 salt solution and this weight was confirmed by titration, which showed a very general concordance giving added proof of the purity of the acids. In dealing with very deliquescent substances, as trichloracetic acid for example, we weighed by difference, making approximate standard solutions rather than exactly N/10 strengths; but even in this case we obtained confirmation of our work. The nondeliquescent, crystalline acids were weighed on a watch crystal, the deliquescent ones in glass stoppered weighing bottles; but in both cases the acids were washed through a funnel into the 100 c.c. measuring flasks with conductivity alcohol, and made up to mark at 25°. Several salts of N/50 dilution were made up in this same manner at the beginning of our work, but this dilution was omitted later as unnecessary.

Let us notice a few of the necessary steps in the titrations. All such were made in 70 c.c. solution.(50 c.c. water, 10 c.c. acid and approximately 10 c.c. ethylate). The carbon dioxide freed air was allowed to bubble through the solution for two minutes before titration. It was found that the presence of some alcohol retarded the endpoint and a number of titrations were made throughout the year to enable us to correct for this. We found as result of our work:



70 c.c. water & 0 c.c. alcohol required .03 c.c. to produce color.

60 c.c. water & 10 c.c. alcohol required .04 c.c.

50 c.c. water & 20 c.c. alcohol required .06 c.c.

Therefore it was necessary to apply this correction as our accuracy in titration was made to check to .02 c.c.

After calculating the amounts necessary, 100 c.c. N/100 salt solution in absolute alcohol at 25° was prepared, placed in a 150 c.c. glass stoppered Erlenmeyer flask, and sealed with rubber cement until the conductivities were to be determined. It was possible to make up three or four different mother solutions of various organic salts in one day, another day being devoted to the dilution down to weaker concentrations, measurement of the conductivities and calculation of results for each salt. These last three operations on a single salt at various dilutions we have designated as a "run".

It is deemed advisable at this point to introduce an example of the calculations upon which a single salt was prepared as described above.

Acid Orthonitrobenzoic  $C_7H_5O_4N$ .

Strength of standard HCl 0.10027.



## I. Standardization of the Ethylate.

10.005 c.c. HCl used in each titration.

## Ethylate Burette

| Readings   | Corrected  | Difference |
|------------|------------|------------|
| 2.77 c.c.  | 2.76 c.c.  |            |
| 10.84 c.c. | 10.83 c.c. | 8.07 c.c.  |
| 10.85 c.c. | 10.84 c.c. |            |
| 18.91 c.c. | 18.92 c.c. | 8.08 c.c.  |
| 18.92 c.c. | 18.93 c.c. |            |
| 26.99 c.c. | 27.02 c.c. | 8.09 c.c.  |

Mean 8.08 less .04 correction = 8.04 c.c. ethylate.

$$10.005:8.04::x::10027$$

$$x = .1248 \text{ normality of the ethylate}$$

To make 100 c.c. N/100 salt solution requires 8.015 c.c.

## II. Standardization of the Organic Acid.

10.005 c.c. acid used in each titration.

## Ethylate Burette

| Readings   | Corrected  | Difference |
|------------|------------|------------|
| 1.98 c.c.  | 1.98 c.c.  |            |
| 10.03 c.c. | 10.02 c.c. | 8.04 c.c.  |
| 10.03 c.c. | 10.02 c.c. |            |
| 18.05 c.c. | 18.07 c.c. | 8.05 c.c.  |
| 18.05 c.c. | 18.07 c.c. |            |
| 26.68 c.c. | 26.11 c.c. | 8.04 c.c.  |



Mean 8.04 less .04 correction = 8.00 c.c. ethylate.

$$8.04 : 8.00 :: .10027 : x$$

$$x = .09977 \text{ normality of organic acid}$$

To make 100 c.c. N/100 salt solution requires 10.02 c.c. plus .01 c.c. excess equals 10.03 c.c.

It should be mentioned that this work was carried on in a rather small room with one window and one door at opposite ends of the room, so that with care it was possible to keep the room temperature at 25° with less than 0.3° variation. Thus it was possible to measure out the solutions in burettes and pipettes provided that such were not handled unnecessarily to cause heating and were always kept dry to prevent cooling in evaporation. All burettes and pipettes were connected with calcium chloride - soda lime tubes to prevent contamination from moisture and carbon dioxide.

In handling the "run" the N/100 solution of one of the salts served as a basis for the preparation of all the more dilute solutions. The following scheme represents the method by which these solutions were prepared.

| $N/100$  |                     |          |                     |                      |
|----------|---------------------|----------|---------------------|----------------------|
| 200 c.c. | $\frac{1}{5}$ soln. | 200 c.c. | $\frac{1}{5}$ soln. | 100 c.c.             |
| 50 c.c.  |                     | 100 c.c. |                     | $\frac{1}{10}$ soln. |
| $N/250$  |                     | $N/500$  |                     | $N/1000$             |
|          |                     |          |                     | $N/2000$             |



40 c.c.  $\left[ \begin{array}{l} \text{to} \\ \text{100 c.c.} \end{array} \right]$  soln.

$\frac{N}{5000}$

20 c.c.  $\left[ \begin{array}{l} \text{to} \\ \text{100 c.c.} \end{array} \right]$  soln.

$\frac{N}{10000}$

10 c.c.  $\left[ \begin{array}{l} \text{to} \\ \text{400 c.c.} \end{array} \right]$  soln.

$\frac{N}{20000}$

After a number of experiments it was deemed inadvisable to wash the measuring flasks with water; they were therefore rinsed with a good grade of alcohol and then three times with conductivity alcohol. The cells were filled with conductivity water until several hours before use. They were then rinsed three times with good alcohol. Each cell was finally washed three times with the solution of the particular dilution to be "run" in that cell before filling. These cells together with one containing the conductivity alcohol were then introduced into the  $15^{\circ}$  bath, gently agitated twice within an hour's time to insure absence of bubbles as well as to hasten diffusion, and then read. They were placed successively in the  $25^{\circ}$  and  $35^{\circ}$  baths allowing for the same time and procedure as in the  $15^{\circ}$  bath.

It will be remembered that the solutions were made up at  $25^{\circ}$ , and that the molecular conductivities were measured at  $15^{\circ}$ ,  $25^{\circ}$  and  $35^{\circ}$ . Alcohol has such an appreciable temperature coefficient of expansion that it was necessary to correct for the contraction and expansion at the other



temperatures. One liter of alcohol at  $25^{\circ}$  expands to 1.01114 liters at  $35^{\circ}$ , and contracts to 0.98923 liter at  $15^{\circ}$ . Therefore to obtain the molecular conductivity at  $35^{\circ}$  one must multiply the specific conductivity at that temperature by the product of the molecular volume and the factor 1.01114. Likewise, to obtain the molecular conductivity at  $15^{\circ}$  the specific conductivity at that temperature must be multiplied by the product of the molecular volume and the factor 0.98923.

#### MEASUREMENTS.

-:-

#### Explanation of Tables.

In the following tables  $V$  signifies the volume at which a solution was made up, and  $\Lambda$  the molecular conductivity of that solution at the various temperatures. The method of calculating  $\Lambda$  is thoroughly familiar. Corrections were applied as described allowing for the contraction and expansion of the solutions. (The solutions were so dilute that their volume changes with variation in temperature were assumed to be the same as that of pure alcohol). The values of  $\Lambda_{-25^{\circ}}$ , therefore, represent the molecular conductivity of a solution of volume  $V$  at  $25^{\circ}$ . The values of  $\Lambda_{-15^{\circ}}$  and  $\Lambda_{-35^{\circ}}$ , however, represent the molecular conductivity of a solution of volume 0.98923  $V$ .



at  $15^{\circ}$  and 1.01114 V at  $35^{\circ}$ . Only the one value V is given in the tables to save space.

All conductivities are expressed in reciprocal ohms.

Concerning the calculation of the temperature coefficients of conductivity, we have adopted this expression -

$$T = \frac{\Lambda \cdot t' - \Lambda \cdot t}{t' - t}$$

where  $\Lambda \cdot t'$  and  $\Lambda \cdot t$  represent the molecular conductivities of the same solution at  $t'$  and  $t^{\circ}$  ( $t' > t$ ), and T the temperature coefficient of conductivity. To find the percentage coefficient of conductivity we have used the formula -

$$\Delta = \frac{T'}{\Lambda \cdot t}$$

where  $\Delta$  is the percentage coefficient and  $\Lambda \cdot t$  the conductivity at the lower temperature. At first the values of  $\Lambda \cdot t$  and  $\Lambda \cdot t'$  at  $15^{\circ}$  and  $35^{\circ}$  were corrected for the difference in volume between 0.98923 V and V, and 1.01114 V and V, respectively. This was done in order that comparison might be made between solutions of the same volume. Later this correction was omitted because of its small value.



Table VII.  
Sodium Formate.

| V.    | $\Delta 25^{\circ}$ | $\Delta 35^{\circ}$ | $\Delta 25^{\circ}-35^{\circ}$ |
|-------|---------------------|---------------------|--------------------------------|
| 100   | 20.09               | 22.70               | 1.30                           |
| 250   | 25.03               | 28.53               | 1.40                           |
| 500   | 28.48               | 33.25               | 1.67                           |
| 1000  | 32.62               | 38.13               | 1.69                           |
| 2000  | 35.34               | 41.88               | 1.85                           |
| 5000  | 37.75               | 44.67               | 1.83                           |
| 10000 | 39.02               | 46.35               | 1.88                           |
| 20000 | 39.76               | 47.24               | 1.88                           |

Table VIII.  
Sodium Acetate.

| V.    | $\Delta 25^{\circ}$ | $\Delta 35^{\circ}$ | $\Delta 25^{\circ}-35^{\circ}$ |
|-------|---------------------|---------------------|--------------------------------|
| 100   | 17.20               | 19.10               | 1.10                           |
| 250   | 22.20               | 25.08               | 1.30                           |
| 500   | 26.07               | 29.76               | 1.42                           |
| 1000  | 29.99               | 34.67               | 1.56                           |
| 2000  | 32.80               | 38.54               | 1.75                           |
| 5000  | 35.42               | 41.62               | 1.75                           |
| 10000 | 36.36               | 42.84               | 1.78                           |
| 20000 | 36.79               | 42.95               | 1.67                           |



Table IX.  
Sodium Chloroacetate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 50    | 12.92             | 14.66             | 16.40             | 1.35                       | 1.19                       |
| 100   | 16.15             | 18.45             | 20.74             | 1.42                       | 1.24                       |
| 250   | 20.52             | 23.76             | 26.92             | 1.58                       | 1.33                       |
| 500   | 23.76             | 27.79             | 32.04             | 1.70                       | 1.53                       |
| 1000  | 26.51             | 31.34             | 36.56             | 1.82                       | 1.67                       |
| 2500  | 29.19             | 34.79             | 41.00             | 1.92                       | 1.81                       |
| 5000  | 30.73             | 36.81             | 43.83             | 1.98                       | 1.91                       |
| 10000 | 31.53             | 37.84             | 45.02             | 2.00                       | 1.90                       |

Table X.  
Sodium Dichloroacetate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 100   | 18.12             | 20.84             | 23.67             | 1.50                       | 1.36                       |
| 250   | 22.38             | 26.06             | 29.91             | 1.64                       | 1.48                       |
| 500   | 25.55             | 30.00             | 34.92             | 1.74                       | 1.64                       |
| 1000  | 28.36             | 33.61             | 39.40             | 1.85                       | 1.72                       |
| 2000  | 30.30             | 36.12             | 42.79             | 1.92                       | 1.85                       |
| 5000  | 32.16             | 38.62             | 46.01             | 2.01                       | 1.91                       |
| 10000 | 33.08             | 39.77             | -                 | 2.02                       | -                          |
| 20000 | 33.97             | 40.67             | 48.71             | 1.97                       | 1.98                       |



Table XI.  
Sodium Trichloroacetate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 100   | 19.03             | 22.05             | 25.13             | 1.59                       | 1.40                       |
| 250   | 23.26             | 27.24             | 31.36             | 1.71                       | 1.51                       |
| 500   | 26.18             | 30.94             | 36.10             | 1.82                       | 1.67                       |
| 1000  | 28.80             | 34.31             | 40.31             | 1.91                       | 1.75                       |
| 2000  | 30.36             | 36.40             | 43.04             | 1.99                       | 1.82                       |
| 5000  | 32.24             | 38.79             | 46.12             | 2.03                       | 1.89                       |
| 10000 | 33.02             | 39.84             | 47.39             | 2.07                       | 1.90                       |
| 20000 | 33.71             | 40.54             | 48.39             | 2.03                       | 1.94                       |

Table XIII.  
Sodium Propionate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 100   | 14.68             | 16.50             | 18.18             | 1.24                       | 1.02                       |
| 250   | 18.80             | 21.41             | 23.95             | 1.39                       | 1.19                       |
| 500   | 22.16             | 25.71             | 28.95             | 1.60                       | 1.29                       |
| 1000  | 25.13             | 29.38             | 33.85             | 1.68                       | 1.52                       |
| 2000  | 27.35             | 32.28             | 37.66             | 1.80                       | 1.67                       |
| 5000  | 29.26             | 34.73             | 40.64             | 1.87                       | 1.70                       |
| 10000 | 30.27             | 36.11             | 42.52             | 1.93                       | 1.77                       |
| 20000 | 30.52             | 36.23             | 42.41             | 1.87                       | 1.71                       |



Table XIII.  
Sodium Butyrate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 100   | 14.39             | 16.16             | 17.82             | 1.23                       | 1.03                       |
| 250   | 18.50             | 21.03             | 23.49             | 1.37                       | 1.17                       |
| 500   | 21.79             | 24.97             | 28.37             | 1.46                       | 1.36                       |
| 1000  | 24.74             | 28.89             | 33.30             | 1.68                       | 1.53                       |
| 2000  | 26.93             | 31.80             | 37.07             | 1.81                       | 1.66                       |
| 5000  | 28.95             | 34.29             | 40.16             | 1.84                       | 1.82                       |
| 10000 | 29.85             | 35.67             | 42.06             | 1.95                       | 1.79                       |
| 20000 | 30.27             | 35.98             | 42.41             | 1.89                       | 1.79                       |

Table XIV.  
Sodium Benzoate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 250   | 18.94             | 21.66             | 24.29             | 1.45                       | 1.21                       |
| 500   | 22.11             | 25.66             | 29.21             | 1.61                       | 1.38                       |
| 1000  | 25.03             | 29.40             | 33.93             | 1.75                       | 1.54                       |
| 2000  | 27.00             | 31.99             | 37.39             | 1.85                       | 1.69                       |
| 5000  | 29.18             | 34.78             | 40.83             | 1.92                       | 1.74                       |
| 10000 | 30.01             | 35.80             | 42.29             | 1.92                       | 1.82                       |
| 20000 | 30.41             | 36.18             | 42.64             | 1.90                       | 1.79                       |



Table XV.  
Sodium Orthoamidobenzoate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 100   | 13.19             | 14.84             | 16.37             | 1.25                       | 1.07                       |
| 250   | 17.24             | 19.60             | 21.86             | 1.37                       | 1.15                       |
| 500   | 20.76             | 23.94             | 26.99             | 1.53                       | 1.27                       |
| 1000  | 23.90             | 27.82             | 31.92             | 1.64                       | 1.47                       |
| 2000  | 26.17             | 30.81             | 35.75             | 1.77                       | 1.60                       |
| 5000  | 28.44             | 33.54             | 38.91             | 1.79                       | 1.60                       |
| 10000 | 29.29             | 34.71             | 40.68             | 1.85                       | 1.72                       |
| 20000 | 29.52             | 34.82             | 40.50             | 1.80                       | 1.63                       |

Table XVI.  
Sodium Orthochlorobenzoate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 100   | 14.54             | 16.49             | 18.34             | 1.34                       | 1.12                       |
| 250   | 18.71             | 21.52             | 24.25             | 1.50                       | 1.27                       |
| 500   | 21.90             | 25.44             | 29.09             | 1.62                       | 1.43                       |
| 1000  | 24.83             | 29.23             | 33.86             | 1.77                       | 1.58                       |
| 2000  | 26.85             | 31.96             | 37.42             | 1.90                       | 1.71                       |
| 5000  | 28.82             | 34.65             | 40.85             | 2.02                       | 1.79                       |
| 10000 | 29.97             | 36.04             | -                 | 2.03                       | -                          |
| 20000 | 30.26             | 36.76             | 43.59             | 2.15                       | 1.86                       |



Table XVII.  
Sodium Metachlorobenzoate.

| v.    | $\Delta 15^{\circ}$ | $\Delta 25^{\circ}$ | $\Delta 35^{\circ}$ | $\Delta 15^{\circ} - 5^{\circ}$ | $\Delta 25^{\circ} - 35^{\circ}$ |
|-------|---------------------|---------------------|---------------------|---------------------------------|----------------------------------|
| 100   | 15.53               | 17.69               | 19.82               | 1.39                            | 1.20                             |
| 250   | 19.74               | 22.76               | 25.80               | 1.53                            | 1.34                             |
| 500   | 22.83               | 26.62               | 30.59               | 1.66                            | 1.49                             |
| 1000  | 25.60               | 30.18               | 35.15               | 1.79                            | 1.65                             |
| 2000  | 27.38               | 32.68               | 38.36               | 1.94                            | 1.74                             |
| 5000  | 29.55               | 35.40               | 41.81               | 1.98                            | 1.81                             |
| 10000 | 30.51               | 36.49               | 43.40               | 1.96                            | 1.89                             |
| 20000 | 31.01               | 37.03               | 43.87               | 1.94                            | 1.85                             |

Table XVIII.  
Sodium Salicylate.

| v.    | $\Delta 15^{\circ}$ | $\Delta 25^{\circ}$ | $\Delta 35^{\circ}$ | $\Delta 15^{\circ} - 5^{\circ}$ | $\Delta 25^{\circ} - 35^{\circ}$ |
|-------|---------------------|---------------------|---------------------|---------------------------------|----------------------------------|
| 50    | 14.19               | 16.32               | 18.42               | 1.51                            | 1.29                             |
| 100   | 17.19               | 19.87               | 22.58               | 1.56                            | 1.36                             |
| 250   | 21.53               | 25.13               | 28.84               | 1.67                            | 1.48                             |
| 500   | 24.56               | 28.92               | 33.60               | 1.78                            | 1.62                             |
| 1000  | 27.48               | 32.62               | 38.31               | 1.87                            | 1.74                             |
| 2000  | 29.18               | 34.87               | 41.18               | 1.95                            | 1.81                             |
| 2500  | 30.00               | 35.92               | 42.45               | 1.97                            | 1.82                             |
| 5000  | 31.20               | 37.47               | 44.57               | 2.01                            | 1.87                             |
| 10000 | 31.90               | 38.38               | 45.61               | 2.03                            | 1.88                             |
| 20000 | 32.38               | 38.99               | 46.36               | 2.04                            | 1.89                             |



Table XIX.  
Sodium Acetylsalicylate.

| V.    | $\Delta 15^{\circ}$ | $\Delta 25^{\circ}$ | $\Delta 35^{\circ}$ | $\Delta 15^{\circ}-25^{\circ}$ | $\Delta 25^{\circ}-35^{\circ}$ |
|-------|---------------------|---------------------|---------------------|--------------------------------|--------------------------------|
| 50    | 14.16               | 16.29               | 18.38               | 1.50                           | 1.28                           |
| 100   | 17.16               | 19.81               | 22.50               | 1.54                           | 1.36                           |
| 250   | 21.50               | 25.08               | 28.71               | 1.67                           | 1.45                           |
| 500   | 24.44               | 28.73               | 33.41               | 1.76                           | 1.63                           |
| 1000  | 27.62               | 32.76               | 38.36               | 1.86                           | 1.71                           |
| 2500  | 30.06               | 35.89               | 42.38               | 1.94                           | 1.81                           |
| 5000  | 31.28               | 37.44               | 44.56               | 1.97                           | 1.90                           |
| 10000 | 32.56               | 38.97               | 46.45               | 1.97                           | 1.92                           |
| 25000 | 32.73               | 39.17               | 46.70               | 1.97                           | 1.92                           |

Table XX.  
Sodium Sulfosalicylate.

| V.    | $\Delta 15^{\circ}$ | $\Delta 25^{\circ}$ | $\Delta 35^{\circ}$ | $\Delta 15^{\circ}-25^{\circ}$ | $\Delta 25^{\circ}-35^{\circ}$ |
|-------|---------------------|---------------------|---------------------|--------------------------------|--------------------------------|
| 50    | 12.38               | 14.28               | 16.21               | 1.53                           | 1.35                           |
| 100   | 15.30               | 17.73               | 20.29               | 1.59                           | 1.44                           |
| 250   | 19.19               | 22.48               | 25.92               | 1.71                           | 1.53                           |
| 500   | 21.92               | 25.90               | 30.22               | 1.82                           | 1.67                           |
| 1000  | 24.34               | 29.00               | 34.11               | 1.95                           | 1.76                           |
| 2000  | 26.12               | 31.27               | 37.11               | 1.97                           | 1.87                           |
| 2500  | 26.58               | 31.93               | 37.86               | 2.01                           | 1.86                           |
| 5000  | 28.18               | 33.88               | 40.42               | 2.02                           | 1.93                           |
| 10000 | 29.37               | 35.47               | 42.41               | 2.08                           | 1.97                           |
| 20000 | 30.65               | 37.13               | 44.16               | 2.11                           | 1.89                           |



Table XXI.  
Sodium Orthonitrobenzoate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 50    | 11.81             | 13.28             | 14.62             | 1.24                       | 1.01                       |
| 100   | 14.79             | 16.73             | 18.59             | 1.31                       | 1.11                       |
| 250   | 18.94             | 21.76             | 24.45             | 1.49                       | 1.24                       |
| 500   | 22.13             | 25.69             | 29.34             | 1.61                       | 1.42                       |
| 1000  | 24.87             | 29.26             | 33.82             | 1.77                       | 1.56                       |
| 2500  | 27.60             | 32.83             | 38.51             | 1.89                       | 1.73                       |
| 5000  | 29.10             | 34.89             | 41.29             | 1.99                       | 1.83                       |
| 10000 | 30.04             | 36.07             | 42.89             | 2.00                       | 1.89                       |

Table XXII.  
Sodium Paranitrobenzoate.

| V.    | $\Delta 15^\circ$ | $\Delta 25^\circ$ | $\Delta 35^\circ$ | $\Delta 15^\circ-25^\circ$ | $\Delta 25^\circ-35^\circ$ |
|-------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| 50    | 14.31             | 16.47             | 18.61             | 1.51                       | 1.30                       |
| 100   | 17.22             | 19.96             | 22.72             | 1.59                       | 1.38                       |
| 250   | 21.04             | -                 | 28.19             | -                          | -                          |
| 500   | 23.98             | 28.36             | 33.09             | 1.83                       | 1.67                       |
| 1000  | 26.59             | 31.69             | 37.30             | 1.84                       | 1.77                       |
| 2500  | 28.63             | 34.25             | 40.51             | 1.96                       | 1.83                       |
| 5000  | 29.75             | 35.66             | 42.53             | 1.99                       | 1.93                       |
| 10000 | 30.70             | 36.98             | 44.10             | 2.05                       | 1.93                       |



Table XXIII.  
Sodium 2,4,dinitrobenzoate.

| V.    | $\Delta$ 15° | $\Delta$ 25° | $\Delta$ 35° | $\Delta$ 15° 25° | $\Delta$ 25° 35° |
|-------|--------------|--------------|--------------|------------------|------------------|
| 100   | 18.20        | 21.09        | 24.09        | 1.59             | 1.42             |
| 250   | 22.18        | 25.98        | 29.93        | 1.71             | 1.52             |
| 500   | 24.95        | 29.45        | 34.39        | 1.80             | 1.69             |
| 1000  | 27.41        | 32.52        | 38.33        | 1.86             | 1.79             |
| 2000  | 28.74        | 34.42        | 40.88        | 1.98             | 1.88             |
| 5000  | 30.45        | 36.63        | 43.71        | 2.03             | 1.93             |
| 10000 | 31.21        | 37.66        | 44.94        | 2.07             | 1.93             |
| 20000 | 31.80        | 38.27        | 45.86        | 2.03             | 1.98             |

Table XXIV.  
Sodium Orthotoluate.

| V.    | $\Delta$ 15° | $\Delta$ 25° | $\Delta$ 35° | $\Delta$ 15° 25° | $\Delta$ 25° 35° |
|-------|--------------|--------------|--------------|------------------|------------------|
| 50    | 11.42        | 12.80        | 14.11        | 1.22             | 1.01             |
| 100   | 14.19        | 16.03        | 17.81        | 1.30             | 1.11             |
| 250   | 18.32        | 21.07        | 23.67        | 1.50             | 1.23             |
| 500   | 21.28        | 24.69        | 28.16        | 1.60             | 1.41             |
| 1000  | 24.53        | 28.80        | 33.24        | 1.74             | 1.54             |
| 2500  | 27.17        | 32.19        | 37.52        | 1.85             | 1.66             |
| 5000  | 28.63        | 34.23        | 40.23        | 1.96             | 1.75             |
| 10000 | 29.56        | 35.36        | 41.75        | 1.96             | 1.81             |



Table XXV.  
Sodium Paratoluate.

| V.    | $\Delta_{15^{\circ}}$ | $\Delta_{25^{\circ}}$ | $\Delta_{35^{\circ}}$ | $\Delta_{15^{\circ} 25^{\circ}}$ | $\Delta_{25^{\circ} 35^{\circ}}$ |
|-------|-----------------------|-----------------------|-----------------------|----------------------------------|----------------------------------|
| 50    | 11.25                 | 12.53                 | 13.74                 | 1.14                             | 0.96                             |
| 100   | 14.05                 | 15.79                 | 17.43                 | 1.24                             | 1.04                             |
| 250   | 18.11                 | 20.68                 | 23.00                 | 1.42                             | 1.12                             |
| 500   | 21.14                 | 24.45                 | 27.75                 | 1.57                             | 1.35                             |
| 1000  | 24.15                 | 28.29                 | 32.55                 | 1.71                             | 1.51                             |
| 2000  | 26.64                 | 31.46                 | 36.62                 | 1.82                             | 1.64                             |
| 5000  | 28.00                 | 33.29                 | 39.21                 | 1.89                             | 1.78                             |
| 10000 | 28.49                 | 33.80                 | 39.91                 | 1.86                             | 1.81                             |

Table XXVI.  
Sodium Picrate.

| V.    | $\Delta_{15^{\circ}}$ | $\Delta_{25^{\circ}}$ | $\Delta_{35^{\circ}}$ | $\Delta_{15^{\circ} 25^{\circ}}$ | $\Delta_{25^{\circ} 35^{\circ}}$ |
|-------|-----------------------|-----------------------|-----------------------|----------------------------------|----------------------------------|
| 100   | 19.77                 | 23.28                 | 27.09                 | 1.78                             | 1.64                             |
| 250   | 24.49                 | 28.93                 | 33.80                 | 1.81                             | 1.68                             |
| 500   | 27.81                 | 33.04                 | 38.79                 | 1.88                             | 1.74                             |
| 1000  | 30.65                 | 36.56                 | 43.24                 | 1.93                             | 1.83                             |
| 2000  | 32.78                 | 39.24                 | 46.60                 | 1.97                             | 1.88                             |
| 5000  | 34.73                 | 41.67                 | 49.85                 | 2.00                             | 1.96                             |
| 10000 | 35.73                 | 42.91                 | 51.46                 | 2.01                             | 1.99                             |
| 20000 | 36.32                 | 43.63                 | 52.43                 | 2.01                             | 2.02                             |
| 40000 | -                     | 43.86                 | -                     | -                                | -                                |



## DISCUSSION OF RESULTS.

The most apparent observation from the foregoing tables is the great similarity in amount of conductivity of these organic salts in alcohol. At 25° in a 1000 liter dilution the extreme limits for the conductivity are from 26 to 36 mhos, with an average conductivity from 28 to 33. The obvious reason for this is the uniform effect of the sodium ion in the solution and the similarity in the velocities of the organic anions. As naturally expected, the conductivities of these salts are much greater than those of the acids.

Very little can be said as to the relation between chemical composition and conductivity. The aliphatic and aromatic derivatives show no difference, and the conductivity of the aromatic compounds seems to be independent of the position of the various substituent groups. Sodium picrate has a much larger conductivity than any other salt, and the monosodiumsulfosalicylate at high dilutions gives abnormally large and increasing conductivities, due probably to the secondary ionization of the carboxyl group at these high dilutions.

In discussing the temperature coefficient of conductivity it is to be noticed that this value becomes gradually larger with increase in dilution, and at the highest dilutions approximates the value 2.00. Just as in the



conductivity results there is here no definite relation between the values for the temperature coefficient and chemical composition.

It is of importance to note that this work on the sodium salts of the organic acids in absolute alcohol has been greatly restricted owing to the almost complete insolubility of a great many of these salts in this solvent. If the work were carried out in alcohol which was not absolute, practically all the salts could be studied, for it is necessary to add a very small amount of water to obtain a sufficient degree of solubility. We have approximately covered the field of available compounds. It is of interest to note that the polybasic acids of both the aliphatic and aromatic series are excluded from study for this reason, as well as all unsaturated acids of both series. A number of salts of aromatic acids with di- and tri-substitutions in the ring were likewise impossible for study.\*

Reference has already been made (see pages 6 - 15) to the work of Heinrich Goldschmidt on the conductivity of alcoholic solutions of sodium salts. We have purposely investigated most of the salts which he studied. A comparison

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\* It was the intention in this department previous to the death of Professor Jones, to extend this work on the salts into the field of mixed solvents (alcohol and water) since a little preliminary work on our part has shown the possibilities of this problem.



of these results is conveniently made by reference to the following tables:

| Salt                   | Goldschmidt  | Author       |
|------------------------|--------------|--------------|
| Sodium Dichloroacetate | Table II p.9 | Table X p.32 |
| " Trichloroacetate     | " I p.9      | " XI p.33    |
| " Salicylate           | " III p.10   | " XVIII p.36 |
| " Sulfosalicylate      | " IV p.10    | " XX p.37    |
| " Picrate              | " V p.11     | " XXVI p.40  |

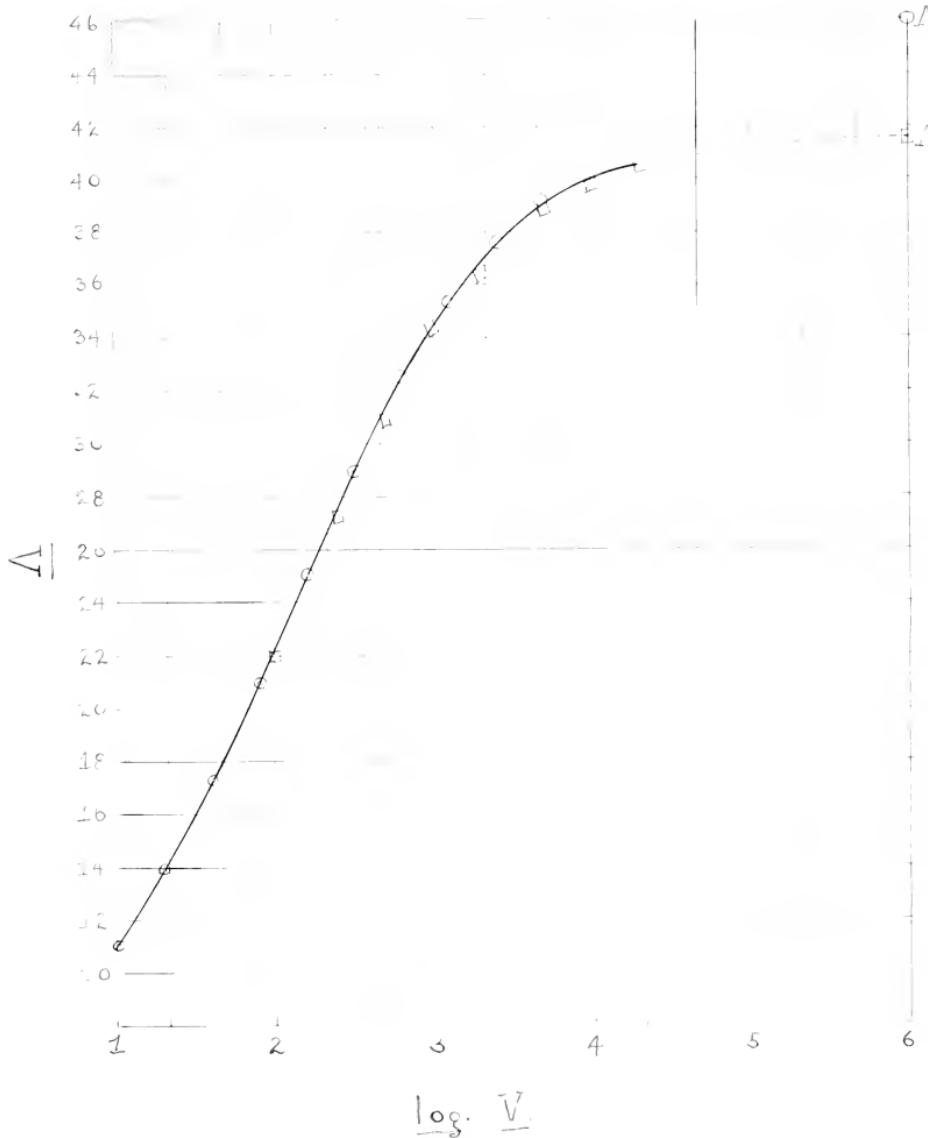
It can be seen from these tables that the two series of conductivity values are in accordance, but an exact comparison cannot be made because of the fact that the values of  $\Delta$  in the two series refer to somewhat different concentrations. In order to make an effective comparison we have plotted the values of  $\Delta$  against the logarithms of the volume  $V$  in the case of sodium trichloroacetate (see Fig. 1). The points circled refer to the data of Goldschmidt, and the squares to that obtained in the present work. With few exceptions all the points lie on one curve, and the slight deviations which occur are within the limits of error of the conductivity method. The four other salts give similar results; therefore their graphs are omitted.

It has been found impossible to obtain a limiting conductivity experimentally, although measurements have been carried out to 10000 and 20000 liter dilutions. It is



Fig. 2

Sodium Trichloroacetate





therefore necessary to determine  $\Delta_0$  by some method of extrapolation. It will be recalled that Goldschmidt used the Kohlrausch formula for this purpose (see page 11), although its applicability to alcoholic solutions and even to aqueous solutions<sup>19</sup> had been previously questioned. We applied this formula to our experimental data with a similarly unsatisfactory result. The calculated values of  $\Delta_0$  vary to such an extent that it is impossible to make a selection.

A function of another form, suggested by A.A.Noyes<sup>20</sup>, which has been successfully used in connection with researches upon the electrical conductivity of aqueous solutions, presented a possible means of determining  $\Delta_0$  in alcoholic solutions. This function has the form -

$$\frac{1}{\Delta} = \frac{1}{\Delta_0} + K(c\Delta)^{n-1}$$

where  $\Delta$  is the equivalent conductance at the concentration  $c$  ( $1/V$ ),  $K$  is a constant, and  $n$  is a number which, for aqueous solutions, lies between 1.3 and 1.7. The value of  $n$  is so chosen that the graph obtained by plotting the reciprocal of the equivalent conductance ( $1/\Delta$ ) at the various concentrations ( $C$ ) against  $(c\Delta)^{n-1}$  is nearly a straight line. Two other graphs corresponding to neighboring values of  $n$ , on opposite sides of the first line, are also drawn

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19. A.A.Noyes, J. Amer. Chem. Soc. 30, 344 (1908).

20. J. Amer. Chem. Soc. 30, 335 (1908).



so as to aid in determining the most probable point at which the graphs cut the  $1/\Delta$  axis <sup>21</sup>. This point is  $1/\Delta_0$ , the reciprocal of the limiting conductivity.

This procedure was followed, using the data at 25° of sodium trichloroacetate, salicylate, orthonitrobenzoate, and 2,4,dinitrobenzoate. The graphs obtained are in every respect similar to those for aqueous solutions, except that the value of  $n$  lies between 1.7 and 1.8. The values of  $\Delta_0$  obtained for the above salts at 25° are -

|                            |      |
|----------------------------|------|
| Sodium trichloroacetate    | 41.6 |
| Sodium salicylate          | 39.9 |
| Sodium orthonitrobenzoate  | 38.0 |
| Sodium 2,4,dinitrobenzoate | 39.2 |

From these figures the percentage dissociation of these salts is obtained by means of the familiar formula -  $\alpha = \frac{1}{\Delta_0}$ .

While the procedure outlined above is thus proved to give satisfactory results in alcoholic solutions, the calculations are quite laborious, and advantage is taken of a much shorter method of approximating  $\Delta_0$ , suggested by Randall <sup>22</sup>. It is a fact that as the zero of concentration (infinite dilution) is approached, the difference in the percentage ionization of all salts approaches zero.

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21. See J. Johnston, J. Amer. Chem. Soc. 31, 1010 (1909).

22. J. Amer. Chem. Soc. 38, 788 (1916).



Randall makes the provisional assumption that the ionization of salts of the same type (such as thallous chloride and potassium chloride) is the same. Knowing the percentage dissociation of potassium chloride at various dilutions very accurately, he calculates the value of  $\Lambda_0$  for thallous chloride by means of the equation -

$$\Lambda_0 = \frac{\Lambda}{\gamma \alpha'}$$

in which  $\alpha'$  is the percentage dissociation of KCl at any given dilution, and  $\Lambda$  the molecular conductivity of TlCl at the same dilution. Such a calculation gives values for  $\Lambda_0$  which approach a constant figure with increasing dilution.

In applying this method to our results we have made use of the values of percentage dissociation obtained by means of the equation of Noyes. It has been found that the four salts sodium trichloroacetate, salicylate, orthonitrobenzoate and 2,4,dinitrobenzoate include examples of all the various types of salts encountered in the present investigation.

The calculated  $\Lambda_0$  is illustrated by the following example:



| V.    | $100\alpha_{50}^o$ | $\Delta_{15}^o$ | $\Delta_{50}$ acetate<br>$\alpha$ -Salicylate |
|-------|--------------------|-----------------|---|
|       | Sod. salicylate    | Sod. acetate    | $\alpha$ -Salicylate                          |
| 100   | 49.8               | 17.20           | 34.5  |
| 250   | 63.0               | 22.20           | 35.2  |
| 500   | 72.5               | 26.97           | 35.9  |
| 1000  | 81.8               | 29.09           | 36.6  |
| 2000  | 87.4               | 32.80           | 37.5  |
| 5000  | 94.0               | 35.42           | 37.7  |
| 10000 | 96.3               | 36.36           | 37.8  |
| 20000 | 97.8               | 36.79           | 37.7  |

Probable  $\Delta_0 = 37.7$



The following table contains the probable values of  $\Delta_e$  at 25° for all the salts studied by the author, calculated in the manner just indicated.

| <u>Sodium</u>      | <u><math>\Delta_e</math></u> | <u>Referred to</u>          |
|--------------------|------------------------------|-----------------------------|
| Formate            | 40.7                         | Salicylate                  |
| Acetate            | 37.7                         | "                           |
| Chloroacetate      | 39.6                         | " & o-NO <sub>2</sub> benz. |
| Dichloroacetate    | 41.4                         | "                           |
| Trichloroacetate   | 41.6                         | -                           |
| Propionate         | 37.1                         | Salicylate                  |
| Butyrate           | 36.9                         | "                           |
| Benzoate           | 37.4                         | " & o-NO <sub>2</sub> benz. |
| Orthoamidobenzoate | 36.6                         | Orthonitrobenzoate          |
| Orthochlorobenz.   | 37.9                         | " & Salicylate              |
| Metachlorobenz.    | 37.9                         | Salicylate                  |
| Salicylate         | 39.9                         | -                           |
| Acetylsalicylate   | 39.9                         | Salicylate                  |
| Sulfosalicylate    | --                           | -                           |
| Orthonitrobenz.    | 38.0                         | -                           |
| Paranitrobenz.     | 38.8                         | Orthonitrobenzoate          |
| 2,4,dinitrobenz.   | 39.2                         | -                           |
| Orthotoluate       | 37.3                         | Orthonitrobenzoate          |
| Paratoluate        | 35.5                         | " & Salicylate              |
| Picrate            | 44.7                         | Dinitrobenzoate             |



## BIOGRAPHY.

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Arthur McCay Pardee, the author of this dissertation, was born in Rochester, New York, March 27, 1885. At an early age he removed with his parents to Pittsburgh, Pennsylvania, and received his preliminary training in the public schools of that city. After receiving his secondary education at the East Liberty Academy, Pittsburgh, Pennsylvania, he entered the freshman class of Washington and Jefferson College, Washington, Pennsylvania, in the fall of 1903. From this institution at graduation he received the degree of Bachelor of Arts in 1907.

During the year 1907-08 he served as Instructor in Chemistry at Tarkio College, Tarkio, Missouri, and in 1908 was appointed Professor of Chemistry at the same institution. In the fall of 1910 he entered The Johns Hopkins University as a graduate student in Chemistry. After a year's graduate work he returned to Tarkio College as Professor of Chemistry and Physics, and occupies that position at the present time. He was given a leave of absence during the year 1915-16 to enable him to extend his graduate studies. His subordinate subjects were Physical Chemistry and Geology.





















